

Title: Nanocomposite Membranes for Hydrogen Separations

Authors: Benny D. Freeman (PI)
Department of Chemical Engineering
University of Texas at Austin
Center for Energy and Environmental Resources
10100 Burnet Road, Building 133
Austin, TX 78758
Tel: (512)232-2803, Fax: (512)232-2807
e-mail: freeman@che.utexas.edu

Students: Scott Matteucci, Haiqing Lin, Roy Raharjo, Scott Kelman

Subcontractor: Lora Toy
RTI International
Center for Energy Technology
3040 Cornwallis Road
Building 11, Bay 2
Research Triangle Park, NC 27709-2194
Tel: (919) 316-3393, Fax: (919) 541-8000
e-mail: ltoy@rti.org

Grant Number: DE-FG26-01NT41277

Period of Performance: September 2001 – September 2004

Date: April 9, 2004

ABSTRACT:

Project Motivation and Objective:

Industrial applications of H₂ are rapidly growing, such as a raw material in refineries and hydrogen powered fuel cells. With increasing demand comes the need to produce and purify H₂ cheaply and efficiently. Currently, steam reforming is used to produce the bulk of H₂ domestically. This reaction produces many by-products that must be removed such as H₂O, CO₂, and CO. Reverse-selective membranes pose an elegant method of removing the more highly condensable steam reformation by-products while maintaining H₂ at high pressure, thus eliminating expensive repressurizing steps.

For reverse-selective membranes to be a realistic method of purifying H₂ certain property thresholds must be met. Foremost is obtaining CO₂/H₂ selectivity of 15 while maintaining sufficient permeability (flux) of CO₂ to render this application economically feasible. Currently no known polymer meets these specifications. Our research group has found that inclusion of

nanoparticles substantially increases gas permeation properties when dispersed into stiff chain, high free volume, glassy polymers (*i.e.* poly (1-trimethylsilyl-1-propyne) [PTMSP])¹. It is our goal to improve the gas transport properties of selected polymers by adding nanoparticles which have the ability to interact selectively with a target gas, thereby increasing CO₂/H₂ selectivity.

Accomplishments to Date

CO₂ is an acid gas, and has been extensively used in catalyst and surface science literature to determine the basicity of metals and metal oxides². MgO has shown a very high affinity for CO₂ adsorption³⁻⁵ as compared to that of H₂⁶. Therefore our research has focused on the incorporation of CO₂ adsorption selective nanoparticles, such as MgO, in polymers already exhibiting reverse-selective characteristics, such as PTMSP.

CO₂ permeability of 20 volume % MgO-filled PTMSP membranes has been observed to be 106,000 Barrers* for at 35°C and pressure 50 psig, an increase of 300% as compared to unfilled PTMSP. MgO-filled PTMSP also shows CO₂ permeability that is 70% higher than fumed silica¹ (particles with acidic characteristics) filled PTMSP membranes of the same loading. It is noteworthy that CO₂/H₂ selectivity of PTMSP does not change with MgO loading. Experiments have shown that MgO does not enhance the sorption capabilities of the nanocomposite film compared to the unfilled PTMSP in regards to acid or inert gases (*i.e.*, N₂).

FTIR and XPS experiments provide evidence suggesting that MgO interacts with the trimethylsilyl group on PTMSP. It is believed that the polymer covers MgO nanoparticle surfaces sufficiently to render any selective adsorption improvement negligible. Thus MgO “adsorbs” the polymer rather than the target gas, which accounts for the stable CO₂/H₂ permeation selectivity experienced by our films. AFM experiments have shown MgO nanoparticles to be better dispersed than equivalent samples of fumed silica. Such dispersion improvements are attributed to the particle-polymer interaction. We believe that improved dispersion of nanoparticles provides the basis for increasing permeability.

PTMSP permeability decreases quickly with time, it is also soluble in most common hydrocarbons. Both of these properties prevent PTMSP from being suitable for industrial applications. Other work has involved stabilization of PTMSP with respect to chemical solubility and aging. PTMSP has been cross-linked to improve membrane insolubility in hydrocarbons and resistance to aging.

$$*1 \text{ Barrer} = 10^{-10} \text{ cm}^3(\text{STP})\cdot\text{cm}/(\text{cm}^2\cdot\text{s}\cdot\text{cmHg})$$

Future Work

Additional research expected to be conducted under this grant includes the following:

- Addition of CO₂ selective nanoparticles to stiff chained low free volume polymers (*i.e.* polyetherimide)
- Addition of MgO for controlled detrimethylsilylation in poly[1-phenyl-2-[p-(trimethylsilyl)phenyl]acetylene], a polymer soluble in hydrocarbons, to form poly(1,2-diphenylacetylene), a polymer insoluble in many hydrocarbons and, therefore, more chemically stable than other substituted acetylene polymers, including PTMSP.

- Exploration of alternative CO₂ adsorption selective nanoparticles (alkaline earth oxides, rare earth oxides)
- Incorporation of nanoparticles into cross-linked PTMSP for aging stability improvement

Papers

T. C. Merkel, L. G. Toy, A. L. Andradý, H. Gracz, and E. O Stejskal, "Investigation of Enhanced Free Volume in Nanosilica-Filled Poly(1-trimethylsilyl-1-propyne) by ¹²⁹Xe NMR Spectroscopy", *Macromolecules*, Vol. 36, 353 (2003).

A. L. Andradý, T. C. Merkel, and L. G. Toy, "Effect of Particle Size on Gas Permeability of Filled Superglassy Polymers", Accepted for publication in *Macromolecules*, In press.

T. C. Merkel, L. G. Toy, and A. L. Andradý, "Gas Permeability of High-Free-Volume Polyacetylenes Containing Polyhedral Oligomeric Silsesquioxane Nanoparticles", In preparation.

Future Presentation

S.T. Matteucci, B.D. Freeman, "Interactions of Basic Nanoparticles with Polyacetylenes and Their Influence Upon Gas Transport and Aging Properties", North American Membrane Society, Honolulu HI, 2004

Students Supported (in part) Under this Grant

- Scott Matteucci, graduate student of the Department of Chemical Engineering, The University of Texas
- Haiqing Lin, graduate student of the Department of Chemical Engineering, The University of Texas
- Roy Raharjo, graduate student of the Department of Chemical Engineering, The University of Texas
- Scott Kelman, graduate student of the Department of Chemical Engineering, The University of Texas

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- (2) Auroux, A.; Gervasini, A. *Journal of Physical Chemistry* 1990, 94, 6371-6379.
- (3) Klabunde, K. J.; Stark, J.; Koper, O.; Mohs, C.; Park, D. G.; Decker, S.; Jiang, Y.; Lagadic, I.; Zhang, D. *Journal of Physical Chemistry* 1996, 100, 12142-12153.
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